Graphene: carbon in two dimensions

Carbon is one of the most intriguing elements in the Periodic Table. It forms many allotropes, some known from ancient times (diamond and graphite) and some discovered 10-20 years ago (fullerenes and nanotubes). Interestingly, the two-dimensional form (graphene) was only obtained very recently, immediately attracting a great deal of attention. Electrons in graphene, obeying a linear dispersion relation, behave like massless relativistic particles. This results in the observation of a number of very peculiar electronic properties – from an anomalous quantum Hall effect to the absence of localization – in this, the first two-dimensional material. It also provides a bridge between condensed matter physics and quantum electrodynamics, and opens new perspectives for carbon-based electronics.

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Carbon plays a unique role in nature. The formation of carbon in stars as a result of the merging of three $\alpha$-particles is a crucial process that leads to the existence of all the relatively heavy elements in the universe. The capability of carbon atoms to form complicated networks is fundamental to organic chemistry and the basis for the existence of life, at least in its known forms. Even elemental carbon demonstrates unusually complicated behavior, forming a number of very different structures. As well as diamond and graphite, which have been known since ancient times, recently discovered fullerenes and nanotubes are currently a focus of attention for many physicists and chemists. Thus, only three-dimensional (diamond, graphite) and zero-dimensional (fullerenes) allotropes of carbon were known. The two-dimensional form was conspicuously missing, resisting any attempt at experimental observation – until recently.

A two-dimensional form of carbon
The elusive two-dimensional form of carbon is named graphene, and, ironically, it is probably the best-studied carbon allotrope theoretically. Graphene – planar, hexagonal arrangements of carbon atoms (Fig. 1) – is the starting point for all calculations on graphite, carbon nanotubes, and fullerenes. At the same time, numerous attempts to synthesize these two-dimensional atomic crystals have usually failed, ending up with nanometer-size crystallites. These difficulties are not surprising in...
light of the common belief that truly two-dimensional crystals cannot exist\(^8\)\(^-\)\(^1\(^2\) (in contrast to the numerous, known quasi-two-dimensional systems). Moreover, during synthesis, any graphene nucleation sites will have very large perimeter-to-surface ratios, thus promoting collapse into other carbon allotropes.

**Discovery of graphene**

In 2004, a group of physicists from Manchester University, UK, led by Andre Geim and Kostya Novoselov, used a very different and, at first glance, even naive approach to obtain graphene and lead a revolution in the field. They started with three-dimensional graphite and extracted a single sheet (a monolayer of atoms) using a technique called micromechanical cleavage\(^1\(^3\)\(^,\)\(^1\(^4\) (Fig. 2). Graphite is a layered material and can be viewed as a number of two-dimensional graphene crystals weakly coupled together — exactly the property used by the Manchester team. By using this top-down approach and starting with large, three-dimensional crystals, the researchers avoided all the issues with the stability of small crystallites. Furthermore, the same technique has been used by the group to obtain two-dimensional crystals of other materials\(^1\(^3\)\(^,\)\(^1\(^4\), including boron nitride, some dichalcogenides, and the high-temperature superconductor Bi-Sr-Ca-Cu-O. This astonishing finding sends an important message: two-dimensional crystals do exist and they are stable under ambient conditions. Amazingly, this humble approach allows easy production of large (up to 100 \(\mu\)m in size), high-quality graphene crystallites, and immediately triggered enormous experimental activity\(^1\(^5\)\(^,\)\(^1\(^6\). Moreover, the quality of the samples produced are so good that ballistic transport\(^1\(^4\) and a quantum Hall effect (QHE) can be observed easily\(^1\(^5\)\(^,\)\(^1\(^6\). The former makes this new material a promising candidate for future electronic applications, such as ballistic field-effect transistors (FETs). However, while this approach suits all research needs, other techniques that provide a high yield of graphene are required for industrial production. Among the promising candidate methods, one should mention exfoliation of intercalated graphitic compounds\(^1\(^7\)\(^-\)\(^2\(^1\) and Si sublimation from SiC substrates, demonstrated recently by Walt de Heer’s group at Georgia Institute of Technology\(^2\(^2\).

**Stability in two dimensions**

The fact that two-dimensional atomic crystals do exist, and moreover, are stable under ambient conditions\(^1\(^7\) is amazing by itself. According to the Mermin-Wagner theorem\(^1\(^2\)\(^,\)\(^1\(^3\), there should be no long-range order in two dimensions. Thus, dislocations should appear in two-dimensional crystals at any finite temperature.

A standard description\(^2\(^3\) of atomic motion in solids assumes that amplitudes of atomic vibration \(u\) near their equilibrium position are much smaller than interatomic distances \(d\), otherwise the crystal would melt according to an empirical Lindemann criterion (at the melting point, \(u \approx 0.1d\)). As a result of this small amplitude, the thermodynamics of solids can be successfully described using a picture of an ideal gas of phonons, i.e. quanta of atomic displacement waves (harmonic approximation). In three-dimensional systems, this view is self-consistent in a sense that fluctuations of atomic positions calculated in the harmonic approximation do indeed turn out to be small, at least at low enough temperatures. In contrast, in a two-dimensional crystal, the number of long-wavelength phonons diverges at low temperatures and, thus, the amplitudes of interatomic displacements calculated in the harmonic approximation diverge\(^8\)\(^-\)\(^1\(^0\).

According to similar arguments, a flexible membrane embedded in three-dimensional space should be crumpled because of dangerous long-wavelength bending fluctuations\(^2\(^4\)\(^-\)\(^2\(^6\). However, in the past 20 years, theorists have demonstrated that these dangerous fluctuations can be suppressed by anharmonic (nonlinear) coupling between bending and stretching modes\(^2\(^4\)\(^-\)\(^2\(^6\). As a result, single-crystalline membranes can exist but should be ‘rippled’. This gives rise to ‘roughness fluctuations’ with a typical height that scales with sample size \(s\) as \(s^{\zeta}\), with \(\zeta \approx 0.6\). Indeed, ripples are observed in graphene, and...
Graphene: carbon in two dimensions

Electronic structure of graphene

The electronic structure of graphene follows from a simple nearest-neighbor, tight-binding approximation. Graphene has two atoms per unit cell, which results in two 'conical' points per Brillouin zone where band crossing occurs, \( K \) and \( K' \). Near these crossing points, the electron energy is linearly dependent on the wave vector. Actually, this behavior follows from symmetry considerations, and thus is robust with respect to long-range hopping processes (Fig. 3).

What makes graphene so attractive for research is that the spectrum closely resembles the Dirac spectrum for massless fermions. The Dirac equation describes relativistic quantum particles with spin \( \frac{1}{2} \); such as electrons. The essential feature of the Dirac spectrum, following from the basic principles of quantum mechanics and relativity theory, is the existence of antiparticles. More specifically, states at positive and negative energies (electrons and positrons) are intimately linked (conjugated), being described by different components of the same spinor wave function. This fundamental property of the Dirac equation is often referred to as the charge-conjugation symmetry. For Dirac particles with mass \( m \), there is a gap between the minimal electron energy, \( E = mc^2 \), and the maximal positron energy, \( -E \) (c is the speed of light). When the electron energy \( E \) is much larger than the thermal energy \( k_BT \), so, in practice, this restriction is not very serious for strongly bonded two-dimensional crystals like graphene.

The Dirac-like spectrum, rather than the usual Schrödinger equation for non-relativistic quantum particles, can be seen as a consequence of graphene’s crystal structure. This consists of two equivalent carbon sublattices A and B (see Fig. 4). Quantum-mechanical hopping between the sublattices leads to the formation of two energy bands, and their intersection near the edges of the Brillouin zone yields the conical energy spectrum. As a result, quasiparticles in graphene exhibit a linear dispersion relation \( E = \hbar k \upsilon_F \), as if they were massless relativistic particles (for example, photons) but the role of the speed of light is played here by the Fermi velocity \( \upsilon_F \approx c/300 \). Because of the linear spectrum, one can expect that quasiparticles in graphene behave differently from those in conventional metals and semiconductors, where the energy spectrum can be approximated by a parabolic (free-electron-like) dispersion relation.

Fig. 3 Band structure of graphene. The conductance band touches the valence band at the \( K \) and \( K' \) points.

Fig. 4 Crystallographic structure of graphene. Atoms from different sublattices (A and B) are marked by different colors.
Chiral Dirac electrons

Although graphene’s linear spectrum is important, it is not the spectrum’s only essential feature. Above zero energy, the current-carrying states in graphene are, as usual, electron-like and negatively charged. At negative energies, if the valence band is not full, unoccupied electronic states behave as positively charged quasiparticles (holes), which are often viewed as a condensed matter equivalent of positrons. Note, however, that electrons and holes in condensed matter physics are normally described by separate Schrödinger equations, which are not in any way connected (as a consequence of the so-called Seitz sum rule34, the equations should also involve different effective masses). In contrast, electron and hole states in graphene should be interconnected, exhibiting properties analogous to the charge-conjugation symmetry in quantum electrodynamics (QED)31-33.

For the case of graphene, the latter symmetry is a consequence of the crystal symmetry, because graphene’s quasiparticles have to be described by two-component wave functions, which are needed to define the relative contributions of the A and B sublattices in the quasiparticles’ make-up. The two-component description for graphene is very similar to the spinor wave functions in QED, but the ‘spin’ index for graphene indicates the sublattice rather than the real spin of the electrons and is usually referred to as pseudospin $\sigma$. This allows one to introduce chirality — formally a projection of pseudospin on the direction of motion — which is positive and negative for electrons and holes, respectively.

The description of the electron spectrum of graphene in terms of Dirac massless fermions is a kind of continuum-medium description applicable for electron wavelengths much larger than interatomic distances. However, even at these length scales, there is still some retention of the structure of the elementary cell, that is, the existence of two sublattices. In terms of continuum-field theory, this can be described only as an internal degree of freedom of the charge carriers, which is just the chirality.

This description is based on an oversimplified nearest-neighbor tight-binding model. However, it has been proven experimentally that charge carriers in graphene do have this Dirac-like gapless energy spectrum15,16. This was demonstrated in transport experiments (Fig. 5) via investigation of the Schubnikov-de Haas effect, i.e. resistance oscillations at high magnetic fields and low temperatures.

Anomalous quantum Hall effect

Magneto-oscillation effects, such as the de Haas-van Alphen (oscillations of magnetization) or Schubnikov-de Haas (magneto-oscillations in resistance) effects, are among the most straightforward and reliable tools to investigate electron energy spectra in metals and semiconductors15. In two-dimensional systems with a constant magnetic field $B$ perpendicular to the system plane, the energy spectrum is discrete (Landau quantization). In the case of massless Dirac fermions, the energy spectrum takes the form (see34, for example):

$$E_{\nu\sigma} = \pm \sqrt{\hbar v_F (\nu + \frac{1}{2})}$$

where $\nu$ is the quantum number, and the term with $\pm\frac{1}{2}$ is connected with the chirality (Fig. 6). For comparison, in the usual case of a parabolic dispersion relation, the Landau level sequence is $E = h_\omega_c \nu (\nu + \frac{1}{2})$ where $\omega_c$ is the frequency of electron rotation in the magnetic field (cyclotron frequency)35.

By changing the value of the magnetic field at a given electron concentration (or, vice versa, electron concentration for a given magnetic field), one can tune the Fermi energy to coincide with one of the Landau levels. This drastically changes all properties of metals (or semiconductors) and, thus, different physical quantities will oscillate with the value of the inverse magnetic field. By measuring the period
of these oscillations, we obtain information about the area \( A \) inside the Fermi surface (for two-dimensional systems, this area is just proportional to the charge-carrier concentration \( n \)). The amplitude of the oscillations allows us to measure the effective cyclotron mass which is proportional to \( \Delta E / B \). For the case of massless Dirac fermions (linear dependence of the electron energy on its momentum), this quantity should be proportional to \( -i \), which was exactly the behavior reported simultaneously by the Manchester researchers\(^{15}\) and Philip Kim and Horst Stormer’s group at Columbia University\(^{16}\) (Fig. 7).

An important peculiarity of the Landau levels for massless Dirac fermions is the existence of zero-energy states (with \( \nu = 0 \) and a minus sign in eq. 1). This situation differs markedly from conventional semiconductors with parabolic bands where the first Landau level is shifted by \( \hbar \omega_c \). As shown by the Manchester and Columbia groups\(^{11,12}\), the existence of the zero-energy Landau level leads to an anomalous QHE with half-integer quantization of the Hall conductivity (Fig. 8, top), instead of an integer one (for a review of the QHE, see\(^{37}\), for example). Usually, all Landau levels have the same degeneracy (number of electron states with a given energy), which is proportional to the magnetic flux through the system. As a result, the plateaus in the Hall conductivity corresponding to the filling of first \( \nu \) levels are integers [in units of the conductance quantum \( e^2/h \)]. For the case of massless Dirac electrons, the zero-energy Landau level has half the degeneracy of any other level (corresponding to the minus sign in eq. 1), whereas each \( p \nu \) level with \( p \geq 1 \) is obtained twice, with \( \nu = p \) and a minus sign, and with \( \nu = p - 1 \) and a plus sign. This anomalous QHE is the most direct evidence for Dirac fermions in graphene\(^{15,16}\).

**Index theorem**

The deepest view on the origin of the zero-energy Landau level, and thus the anomalous QHE is provided by an Atiyah-Singer index theorem that plays an important role in modern quantum field theory and theory of superstrings\(^{38}\). The Dirac equation has charge-conjugation symmetry between electrons and holes. This means that, for any electron state with a positive energy \( E \), a corresponding conjugated hole state with energy \( -E \) should exist. However, states with zero energy can be, in general, anomalous. For curved space (e.g. for a deformed graphene sheet with some defects in crystal structure) and/or in the presence of so-called “gauge fields” (electromagnetic fields provide the simplest example of these fields), sometimes the existence of states with zero energy is guaranteed for topological reasons, these states being chiral. (In the case of graphene, this means that, depending on the sign of the magnetic field, only sublattice A or sublattice B states contribute to the zero-energy Landau level.) In particular, this means that the number of these states expressed in terms of total magnetic flux is a topological invariant and remains the same even if the magnetic field is inhomogeneous\(^{15}\). This is an important conclusion since the ripples on graphene create effective inhomogeneous magnetic fields with magnitudes up to 1 T, leading to suppression of the weak localization\(^{27}\). However, because of these topological arguments, inhomogeneous magnetic fields cannot destroy the anomalous QHE in graphene. For further insight into the applications of the index theorem to two-dimensional systems, and to graphene in particular, see\(^{39,40}\).

**Quasiclassical considerations**

An alternative view of the origin of the anomalous QHE in graphene is based on the concept of a “Berry phase”\(^{41}\). Since the electron wave
function is a two-component spinor, it has to change sign when the electron moves along a closed contour. Thus, the wave function gains an additional phase $\phi = \pi$. In quasiclassical terms (see44,45, for example), stationary states are nothing but electron standing waves and they can exist if the electron orbit is, at least, half the wavelength. As a result of the additional phase shift by the Berry phase, this condition is already satisfied for the zeroth length of the orbit, that is, for zero energy! Other aspects of the QHE in graphene are considered elsewhere46-48.

**Anomalous QHE in bilayer graphene**

In relativistic quantum mechanics, chirality is intimately connected with relativistic considerations that dictate, at the same time, the linear energy spectrum for massless particles. The discovery of graphene also opens a completely new opportunity to investigate chiral particles with a parabolic (nonrelativistic) energy spectrum! This is the case for bilayer graphene47.

For two carbon layers, the nearest-neighbor tight-binding approximation predicts a gapless state with parabolic bands touching at the $K$ and $K'$ points, instead of conical bands47,48. More accurate consideration49 gives a very small band overlap (about 1.6 meV) but, at larger energies, bilayer graphene can be treated as a gapless semiconductor. At the same time, the electron states are still characterized by chirality and by the Berry phase (equal, in this case, to $2\pi$ instead of $\pi$). Exact solution of the quantum mechanical equation for this kind of spectrum in the presence of a homogeneous magnetic field gives the result50,51 $E = \sqrt{\nu E_F}$ and, thus, the number of states with zero energy ($\nu = 0$ and $\nu = 1$) is twice that of monolayer graphene. As a result, the QHE for bilayer graphene differs from both single-layer graphene and conventional semiconductors, as found experimentally47 (Fig. 8, bottom).

**Tunneling of chiral particles**

The chiral nature of electron states in bilayer, as well as single-layer, graphene is of crucial importance for electron tunneling through potential barriers, and thus the physics of electronic devices such as ‘carbon transistors’52.

**Quantum tunneling**

Quantum tunneling is a consequence of very general laws of quantum mechanics, such as the Heisenberg uncertainty relations. A classical particle cannot propagate through a region where its potential energy is higher than its total energy (Fig. 9). However, because of the uncertainty principle, it is impossible to know the exact values of a quantum particle’s coordinates and velocity, and thus its kinetic and potential energy, at the same time instant. Therefore, penetration through the ‘classically forbidden’ region turns out to be possible. This phenomenon is widely used in modern electronics, beginning with the pioneering work of Esaki53.

Klein paradox

When a potential barrier is smaller than the gap separating electron and hole bands in semiconductors, the penetration probability decays exponentially with the barrier height and width. Otherwise, resonant tunneling is possible when the energy of the propagating electron coincides with one of the hole energy levels inside the barrier. Surprisingly, in the case of graphene, the transmission probability for normally incident electrons is always equal to unity, irrespective of the height and width of the barrier54-56. In QED, this behavior is related to the Klein paradox50,54-56. This phenomenon usually refers to a counterintuitive relativistic process in which an incoming electron starts penetrating through a potential barrier, if the barrier height exceeds twice the electron’s rest energy $mc^2$. In this case, the transmission probability $T$ depends only weakly on barrier height, approaching perfect transparency for very high barriers, in stark contrast to conventional, nonrelativistic tunneling. This relativistic effect can be attributed to the fact that a sufficiently strong potential, being repulsive for electrons, is attractive to positrons, and results in positron states inside the barrier. These align in energy with the electron continuum outside the barrier. Matching between electron and positron wave functions across the barrier leads to the high-probability tunneling described by the Klein paradox. In other words, it reflects an essential difference between nonrelativistic and relativistic quantum mechanics. In the former case, we can measure accurately either the position of the electron or its velocity, but not both simultaneously. In relativistic quantum mechanics, we cannot measure even electron position with arbitrary accuracy since, if we try to do this, we create electron-positron pairs from the vacuum and we cannot distinguish our original electron from these newly created electrons.

Graphene opens a way to investigate this counterintuitive behavior in a relatively simple benchtop experiment, whereas previously the Klein paradox was only connected with some very exotic phenomena, such as superconductivity.
Graphene: carbon in two dimensions

Tunneling in bilayer graphene

From the point of view of applications, the Klein paradox is rather bad news since it means that a ‘carbon transistor’ using single-layer graphene cannot be closed by any external gate voltage. In contrast, it has been shown that chiral tunneling in the case of a bilayer leads to even stronger suppression of the normally incident electron penetration (Fig. 10) than in conventional semiconductors[50]. By creating a potential barrier (with an external gate), one can manipulate the transmission probability for ballistic electrons in bilayer graphene. At the same time, there is always some ‘magic angle’ where the penetration probability equals unity (Fig. 10), which also should be taken into account in the design of future carbon-based electronic devices.

Absence of localization

The tunneling anomalies in single- and bilayer graphene systems are expected to play an important role in their transport properties, especially in the regime of low carrier concentrations where disorder induces significant potential barriers and the systems are likely to split into a random distribution of p-n junctions. In conventional two-dimensional systems, sufficiently strong disorder results in electronic states that are separated by barriers with exponentially small transparency[57,58]. This is known to lead to Anderson localization. In graphene, this can be avoided for small external gate voltages (Fig. 10). The difference in the Fermi energies for the red and blue curves, respectively (concentrations that are typical of most experiments with graphene). This corresponds to a Fermi energy $E_F$ of the incident electrons of $\approx 80$ meV and 17 meV for single- and bilayer graphene, respectively, and $\lambda = 50$ nm. The barrier heights are (a) $200$ meV and (b) $50$ meV (red curves), and (a) $285$ meV and (b) $100$ meV (blue curves).

Fig. 10 Transmission probability $T$ through a 100 nm wide barrier as a function of the incident angle for (a) single- and (b) bilayer graphene. The electron concentrations outside the barrier are chosen as $0.5 \times 10^{12}$ cm$^{-2}$ for all cases. Inside the barrier, hole concentrations $p$ are $1 \times 10^{12}$ and $3 \times 10^{12}$ cm$^{-2}$ for the red and blue curves, respectively (concentrations that are typical of most experiments with graphene). This corresponds to a Fermi energy $E_F$ for the incident electrons of $\approx 80$ meV and 17 meV for single- and bilayer graphene, respectively, and $\lambda = 50$ nm. The barrier heights are (a) $200$ meV and (b) $50$ meV (red curves), and (a) $285$ meV and (b) $100$ meV (blue curves).

Graphene devices

The unusual electronic properties of this new material make it a promising candidate for future electronic applications. Mobilities that are easily achieved at the current state of ‘graphene technology’ are $\approx 20,000$ cm$^2$/V·s, which is already an order of magnitude higher than that of modern Si transistors, and they continue to grow as the quality of samples improves. This ensures ballistic transport on submicron distances – the holy grail for any electronic engineer.

Probably the best candidates for graphene-based FETs will be devices based on quantum dots and those using p-n junctions in bilayer graphene[59,60].

Another promising direction for investigation is spin-valve devices. Because of negligible spin-orbit coupling, spin polarization in graphene survives over submicron distances, which has recently allowed observation of spin-injection and a spin-valve effect in this material[61]. It has also been shown by Morpurgo and coworkers at Delft University[62] that superconductivity can be induced in graphene through the proximity effect (Fig. 11). Moreover, the magnitude of the supercurrent can be controlled by an external gate voltage, which can be used to create a superconducting FET.

While these applications mentioned are a focus for further investigation, there are some areas where graphene can be used straightaway. Gas sensors is one. The Manchester group[63] has shown that graphene can absorb gas molecules from the surrounding atmosphere, resulting in doping of the graphene layer with electrons or holes depending on the nature of the absorbed gas. By monitoring...
changes in resistivity, one can sense minute concentrations of certain gases present in the environment.

Conclusions

It is impossible to review all aspects of graphene physics and chemistry here. We hope, however, that the above examples demonstrate graphene’s great interest for both fundamental research (where it forms a new, unexpected bridge between condensed matter and quantum field theory) and possible applications. Graphene is the first example of a truly two-dimensional crystal. This opens many interesting questions concerning the thermodynamics, lattice dynamics, and structural properties of such systems. Being a gapless semiconductor with a linear energy spectrum, single-layer graphene realizes a two-dimensional, massless Dirac fermion system that is of crucial importance for understanding unusual electronic properties, such as an anomalous QHE, absence of the Anderson localization, etc. Bilayer graphene has a very unusual, gapless, parabolic spectrum, giving a system with an electron wave equation that is different from both Dirac and Schrödinger systems. These peculiarities are important for developing new electronic devices such as carbon transistors.

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